

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 899 779 A2**

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:

03.03.1999 Bulletin 1999/09

(51) Int Cl.<sup>6</sup>: **H01L 21/285**

(21) Application number: **98306924.6**

(22) Date of filing: **28.08.1998**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**

Designated Extension States:

**AL LT LV MK RO SI**

(72) Inventors:

• **Lu, Jlong-Ping**

**Dallas, Texas 75243 (US)**

• **Cho, Chih-Chen**

**Richardson, Texas 75082 (US)**

(30) Priority: **28.08.1997 US 920303**

(71) Applicant: **TEXAS INSTRUMENTS**

**INCORPORATED**

**Dallas Texas 75265 (US)**

(74) Representative: **Darby, David Thomas et al**

**Abel & Imray,**

**20 Red Lion Street**

**London WC1R 4PQ (GB)**

(54) **Method for fabricating thermally stable contacts**

(57) In order to provide a thermally stable diffusion barrier for a contact, a layer of titanium (11) is formed on the patterned substrate (10). A layer of tungsten nitride (12) is formed on the titanium layer (11). After an annealing step, an interfacial layer (11') and a layer of

titanium nitride (12') are formed between the substrate (10) and a tungsten layer (13'). These layers provide a diffusion barrier which is more thermally stable than a titanium nitride layer applied directly on the substrate and which permits the formation of a contact structures that can withstand subsequent high temperature steps.



**FIG. 1A**

**EP 0 899 779 A2**

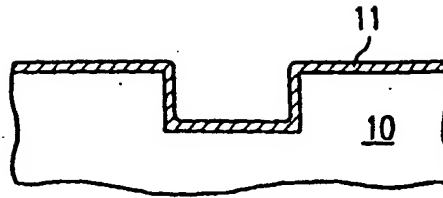


FIG. 1B

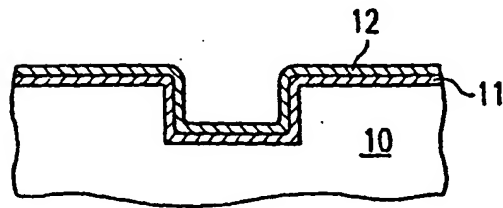


FIG. 1C

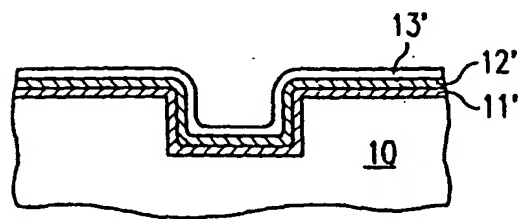


FIG. 1D

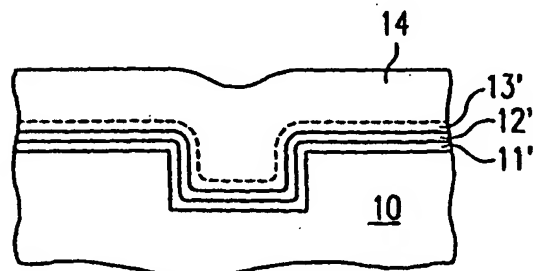


FIG. 1E

## Description

[0001] This invention relates generally to the fabrication of semiconductor devices and, more particularly, to an improved contact structure for semiconductor devices which can withstand the high-temperature processes necessary at later stages of device fabrication flow.

[0002] As the density of integrated devices in dynamic random access memory (DRAM) devices has increased, the size of the contact hole has decreased while the aspect ratio of the contact hole has increased. As a result, the fabrication of contact structures for sub-micron complementary metal oxide semiconductor (CMOS) devices is difficult. Typically, a contact structure is formed after the formation of the capacitor elements. However, if the contact structure can be formed before the formation of the capacitor structure and withstand the high temperature steps required in the formation of the capacitor structure(s), the process flow can be simplified and a reduced aspect ratio for the contact hole(s) can be obtained. In the prior art, a TiN diffusion barrier between the tungsten conducting layer and the substrate is formed by sputtering titanium in an ambient environment which includes nitrogen or by chemical vapor deposition. The Ti/TiN materials can not withstand a high temperature cycle at temperatures required for the formation of a capacitor structure.

[0003] A need has been felt for a technique for forming a contact with a diffusion barrier which is easy to fabricate and which has sufficient thermal stability to withstand the process temperature required in the formation of contact structures.

[0004] An illustrative embodiment of the present invention seeks to provide a method for forming a contact that avoids or minimizes above mentioned problems.

[0005] Aspects of the invention are specified in the claims. In carrying out principles of the present invention a contact is formed by first forming, after the contact patterns are fabricated, a titanium layer. The titanium layer can be formed, for example, by a chemical vapor deposition or a physical vapor deposition process. A tungsten nitride (WN<sub>x</sub>) is deposited on the titanium layer. The tungsten nitride layer can be formed by thermal, photo- or plasma-enhanced chemical vapor deposition, or by sputtering a tungsten target in an ambient atmosphere containing nitrogen. During a high temperature annealing step, the tungsten nitride layer reacts with the titanium layer. The nitrogen in the tungsten nitride layer can transfer to the titanium layer to form titanium nitride (TiN<sub>x</sub>) layer. The resulting titanium nitride layer provides a more stable (at high temperature) diffusion barrier than the conventional deposited titanium nitride layer.

[0006] For a better understanding of the present invention, reference will now be made, by way of example, to the accompanying drawings, in which:

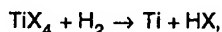
[0007] Figure 1A through Figure 1D illustrate the steps to provide a temperature-stable contact diffusion barrier according to a first embodiment of the present invention.

[0008] Figure 2A through Figure 2E illustrate the process to provide a temperature-stable contact diffusion barrier according to a second embodiment of the present invention.

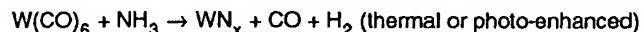
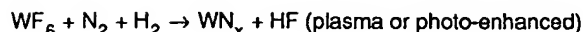
[0009] Referring to Fig. 1A through Fig. 1E, a first procedure for providing a thermally stable contact structure according to the first embodiment of the present invention. In Fig. 1A, a substrate 10 has been patterned. In Fig. 1B, a layer of titanium 11 is formed on substrate 10. In Fig. 1C, a layer of tungsten nitride (WN<sub>x</sub>) 12 is formed on the titanium layer 11. The substrate 10 and layers (11 and 12) formed thereon are then annealed. As a result of the annealing process, titanium layer 11 reacts with the underlying substrate to form an interfacial layer 11', the tungsten nitride layer 12 is converted to titanium nitride (TiN<sub>y</sub>) layer 12', and a tungsten layer 13' is formed on layer 12'. In Fig. 1E, an additional layer of tungsten 14 can be formed on tungsten layer 13.

[0010] Referring to Fig. 2A through Fig. 2E, a second process for forming a thermally stable diffusion barrier is illustrated. In Fig. 2A, a substrate 20 is patterned. In Fig. 2B, a titanium layer 21 is formed on the substrate. In Fig. 2C, a tungsten nitride (WN<sub>p</sub>) layer 22 is formed on titanium layer 21. And a tungsten layer 23 is formed on the tungsten nitride layer 22. The substrate 20 and the layers (21, 22, 23) formed thereon are annealed. As a result of this annealing process, titanium layer 21 is converted to a titanium silicon (TiSi<sub>q</sub>) layer 21', tungsten nitride (WN<sub>p</sub>) layer 22 reacts with the underlying titanium to form titanium nitride (TiN<sub>r</sub>) layer 22', and a tungsten layer 23 remains.

[0011] In the fabrication processes described above, the titanium deposition steps can be performed using chemical vapor deposition processes or physical vapor deposition processes. The preferable chemical vapor deposition process for the titanium deposition is based on the following chemical process



where X = Cl, Br, or I. If the physical vapor deposition process is used, the preferred method is an ionized metal deposition (IMP), the IMP process having better step coverage than conventional sputtering methods. For tungsten nitride deposition, the preferred process is the chemical vapor deposition based on the following chemical processes:



10 [0012] Tests using the x-ray diffraction (XRD) technique or the Rutherford backscattering spectrometry (RBS) technique have demonstrated the thermal stability of the multi-layer structures resulting from the processes described with respect to Figs. 1A-1E and Figs. 2A-2E. For W/TiN/Ti/Si control samples fabricated using the usual techniques,  $\text{WSi}_2$  formation can be detected using the XRD technique and the RBS technique after annealing for 10 minutes at 850°C. In contradistinction, the processes disclosed herein provide no evidence of an interaction between the tungsten and the silicon substrate.

15 [0013] The techniques of the present invention can be implemented in a slightly different form. By way of specific example, the titanium layer can be replaced by  $\text{TiSi}_m$  or  $\text{TiSi}_n/\text{Ti}$  layers. In addition, the titanium and the titanium silicide layers can be replaced by cobalt, nickel and/or the corresponding metal silicides.

20 [0014] While the invention has been described with particular reference to the preferred embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents substituted for elements of the preferred embodiment without departing from the invention. In addition, many modifications may be made to adapt a particular situation and material to a teaching of the present invention without departing from the essential teachings of the present invention.

25 [0015] As is evident from the foregoing discussion, certain aspects of the invention are not limited to the particular details of the examples illustrated, and it is therefore contemplated that other modifications and applications will occur to those skilled in the art. It is accordingly intended that the claims shall cover all modifications and applications as do not depart from the spirit and scope of the invention.

30 [0016] In particular, the invention also provides a process of manufacturing a semiconductor device which includes a method as hereinbefore described and more especially a method as defined in any one of the claims herein, and a semiconductor device made or obtainable by any such process.

#### Claims

35 1. A method of forming a diffusion barrier layer for a contact structure, said method comprising the steps of:

forming a layer of titanium on a patterned substrate;  
forming a layer of tungsten nitride on said titanium layer;  
annealing said layers along with said substrate.

40 2. The method of claim 1 wherein titanium is replaced by an element selected from the group consisting of cobalt and nickel.

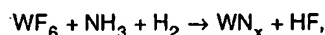
45 3. The method of claim 1 wherein said titanium layer is replaced by an  $\text{MSi}_x$  layer or  $\text{MSi}_x/\text{M}$  layers, wherein M is a metal selected from the group consisting of titanium, cobalt and nickel.

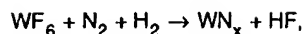
4. The method of claim 1 wherein said titanium layer is formed using a CVD process based on the chemical process



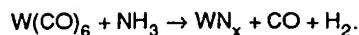
where X is selected from the group consisting of chlorine, bromine and iodine.

55 5. The method of claim 1 wherein said tungsten nitride layer is formed using CVD process based on a chemical process selected from the group of chemical processes consisting of:





and



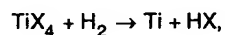
6. A method for forming a contact structure, said method comprising the steps of:

forming a titanium layer on a substrate;  
 forming a tungsten nitride layer on said titanium layer;  
 forming a tungsten layer on said tungsten nitride layer; and  
 annealing the structure resulting from a formation of these layers.

7. The method of claim 8 wherein titanium is replaced by an element selected from the group consisting of cobalt and nickel.

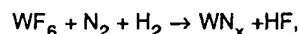
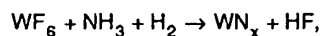
8. The method of claim 8 wherein said titanium layer is replaced by a one of an  $\text{MSi}_x$  layer or a  $\text{MSi}_x/\text{M}$  layers, where M is selected from the group consisting of titanium, cobalt, or nickel.

9. The method of claim 8 wherein said titanium layer is formed using a CVD process based on the chemical process



wherein X is selected from the group consisting of chlorine (Cl), bromine (Br), and iodine (I).

10. The method of claim 8 wherein said tungsten nitride layer is formed using CVD process based on a chemical process selected from the group of chemical processes consisting of:



and

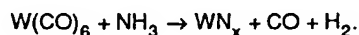




FIG. 1A

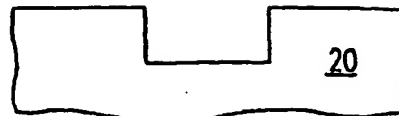


FIG. 2A

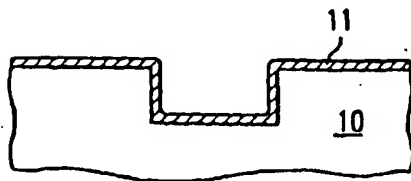


FIG. 1B

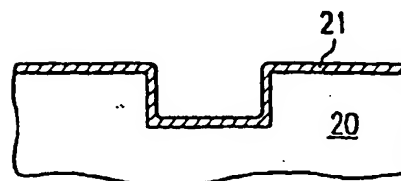


FIG. 2B

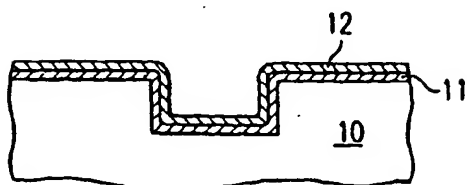


FIG. 1C

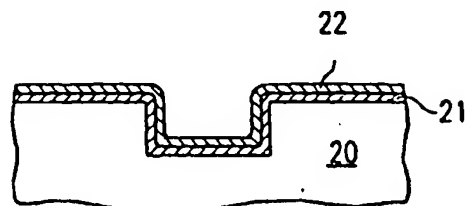


FIG. 2C

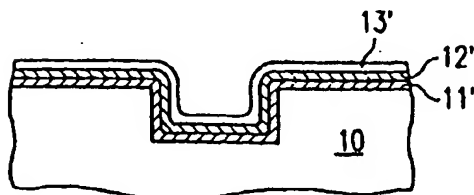


FIG. 1D

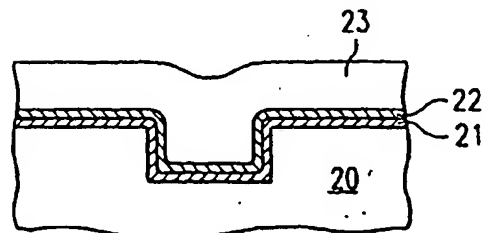


FIG. 2D

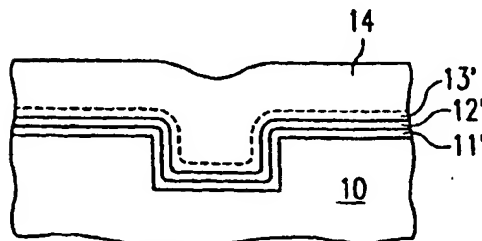


FIG. 1E

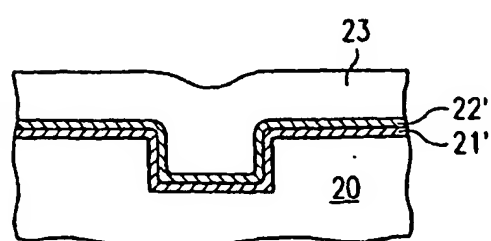


FIG. 2E